(12) UK Patent Application (19) GB (11) 2 158 834 A

(43) Application published 20 Nov 1985

(21) Application No 8512177

(22) Date of filing 14 May 1985

(30) Priority data
(31) 8401570 (32) 16 May 1984 (33) NL

(71) Applicant
DSM Resins BV (Netherlands),
P O Box 615, 8000 AP Zwolle, The Netherlands

(72) Inventors
Hans Pieter Braber
Arie Tinkelenberg

(74) Agent and/or Address for Service
Hyde Heide & O'Donnell,
146 Buckingham Palace Road, London SW1W 9TR

(51) INT CL⁴
C08L 61/06 // C08K 3/30 7/14

(52) Domestic classification
C3R 1C C12 C13M C16 C22 C24 C29 C33A C33X C4 C5B1 C6X C8B L1A L2B L2CX V
U1S 1384 1577 C3R

(56) Documents cited
GB A 2038348 GB 1522995 GB 1037368
GB 1548959

(58) Field of search
C3R
C3K

(54) Thermosetting moulding compounds on the basis of resole

(57) Thermosetting resin composition on the basis of resole, filler and condensation catalysts, possibly with thickener(s), glass fibre and other usual additives. At least a portion of the filler is a water-binding agent which does not become essentially water-binding until above a temperature of 50°C.

The thermosetting resin compositions are preferably used as moulding compounds, such as, in particular 'Bulk moulding compounds' (BMC), 'Dough moulding compounds' (DMC) or 'Sheet moulding compounds' (SMC).

The water-binding agent is suitably gypsum anhydrite.

GB 2 158 834 A

SPECIFICATION

Thermosetting moulding compounds on the basis of resole

The invention relates to thermosetting resin compositions, in particular moulding compounds, on the basis of resole, filler and condensation catalysts, possibly with thickener(s), glass fiber and other usual additives.

Such resin compositions are known from, for example, US Patent Specification No. 4,075,155. However, these known resin compositions give rise to problems during thermosetting on account of the water present in the resole.

In a process for moulding phenolic resin, glass fibre and acid catalysts jointly sprayed into a mould, the Belgian Patent Specification No. 847449 proposes the simultaneous use of a hydrophylic inorganic material, such as $CaSO_4$ hemihydrate or B_2O_3. However, this idea is of no use for ready-for-use moulding compounds as meant in the present application, since a water-withdrawing agent would affect the viscosity stability of the compound itself.

The object of the invention is to provide a thermosetting composition on the basis of resoles which does not have the above-mentioned disadvantages and is therefore suitable for use as a moulding compound.

To this end, according to the invention, in a thermosetting composition on the basis of resole, filler and condensation catalysts and possibly thicknener(s), glass fibre and other usual additives at least a portion of the filler is a water-binding agent which does not become essentially (i.e. substantially) water-binding until above a temperature of 50°C.

According to the invention, such thermosetting compositions are preferably used as moulding compounds, such as, in particularl, 'Bulk Moulding Compounds' (BMC), 'Dough Moulding Compounds' (DMC) or 'Sheet Moulding Compounds' (SMC).

Such processing techniques have been described in, for example, the lectures read during the '13e Offentliche Jahrestagung der Arbeitsgemeinschaft Verstärkte Kungststoffen', October 5–7, 1976.

The thermosetting resin compositions according to the invention preferably contain at least 25 per cent by weight, relative to the resole, of the water-binding agent which is not essentially water-binding until above 50°C.

A very suitable water-binding agent to be used according to the invention is gypsum anhydrite ($CaSO_4 . O\ H_2O$). According to the invention, gypsum anhydrite is preferably used in a ratio of at least 50 per cent by weight relative to the resole.

Additives in moulding compounds according to the invention include, for example, further fillers such as marl, powdered quartz, Millicarb (filler of the firm Plüss Staufer AG), talc etc.; thickeners such as MgO, epoxy resins etc.; mould release agents such as calcium stearate, ACMOS (mould release agent of the firm of Tietjen & Co) and further usual additives. As condensation catalyst, alkalimetal hydroxides and/or carbonates can very suitably be used.

For moulding compounds according to the invention for application according to the sheet moulding technique the following component ratios are preferably applied:
100 parts by weight of resole;
5–25 parts by weight of thickener;
25–200 parts by weight of gypsum anhydrite;
0–150 parts by weight of filler other than gypsum anhydrite;
0–20 parts by weight of water;
10–175 parts by weight of glass fibers;
0–15 parts by weight of condensation catalyst;
and, possibly, other usual additives.

For compositions according to the invention for application according to the bulk moulding technique or the dough moulding technique, the following component ratios are preferably applied:
100 parts by weight of resole;
0–20 parts by weight of thickener;
25–200 parts by weight of gypsum anhydrite;
0–150 parts by weight of filler other than gypsum anhydrite;
0–15 parts by weight of water;
0–25 parts by weight of glass fibres;
0–15 parts by weight of condensation catalyst;
and, possibly, further usual additives.

The invention is explained in more detail by th following examples but is not restricted thereto.

Preparation of resoles.

Example 1

5980 grams of 90% (phenol (the rest being water) are introduced into a reactor provided with a stirrer, a thermometer, a condensor and a heating and cooling coil. After addition of 201 grams of 50% NaOH the mixture is heated.

At about 80°C, dosage of 3819 grams of paraform is started. The temperature quickly rises on account of the exothermic reaction that occurs, and is kept at 95% by cooling. During cooling, paraform dosage is interrupted.

After about 20 minutes all paraform has been added and the reaction is continued for 15 minutes at 95°C. To the resin 200 grams of caprolactam are added, after which the condensation is continued until the desired resin viscosity has been reached (8000 m.Pa.s). The resin is cooled to room temperature. A Resole I is obtained, which is used in moulding compounds according to the examples below.

Example 2

2990 grams of 90% phenol and 100.5 grams of 50% NaOH are introduced into a reactor like the one in Example 1. 1909.5 grams of paraform are dosed in the same manner as in Example 1. After paraform dosage, the condensation is continued at 95°C, the reaction proceeding as follows:

period for which condensation is continued	viscosity	water-compatibility*
20 minutes	1170 mPa.s	5.2
30 minutes	2062 mPa.s	3.1
40 minutes	3375 mPa.s	1.9
50 minutes	6150 mPa.s	1.2

*number of grams of water needed to cause permanent turbidity in 1 gram of resin solution at 20°C.

Next, the temperature of the resin is lowered to 80°C, after which condensation is continued until the resin has reached a viscosity of 10,000 mPa.s. A resole II is obtained, which is used in moulding compounds according to the examples below.

Preparation of sheet moulding compounds

Example 3

2100 grams of phenolic resin (Resole I of Example I), 210 grams of MgO (as thickener), 2100 grams of gypsum anhydrite (product AB 20 of the firm of Bayer), 600 grams of marl (as additional filler), 114 grams of water, 96 grams of calcium stearate (as mould release agent), 50 grams of 50% NaOH solution and 210 grams of 50% K_2CO_3 solution, are mixed to a homogeneous compound in a mixer.

The compounds is still more or less liquid, comparable with a cement mortar.

On an SMC machine a thin layer of compound is spread with a doctor blade on a proceeding polyethylene film. Subsequently, using a cutting device glass roving (30% (wt) glass fibre calculated on the weight of the compound) is strewn on it, after which a second layer of compound, also applied to a polyethylene film, is applied on top. The resulting 'sandwich' of compound glass fibre and compound is further compacted with a number of pressure rolls and a pressure belt so that the glass fibres are moistened by the resin. At the end of the machine sheet—still packed in the polyethylene films—is rolled up.

After the thickening of the compound the polyethylene films can be pulled from the SMC. At this moment a non-sticky flexible sheet (plate) has been obtained.

Parts of this sheet are piled up and put in a hot mould in which they first flow out under heat and pressure until the mould is completely filled and subsequently cure to form the desired product. Moulding conditions are at 160°C; pressure 100 kg/cm², moulding period 3 minutes. The resulting objects are of good quality and show a smooth surface.

Example 4

2000 g of ph nolic r sin (resole II of Example 2), 2600 g of gypsum anhydrite (product AB of the firm of Bayer), 1100 g of Microdol (talc), 300 g of Eurepox (epoxy resin of the firm of Schering), 75 g of Euredur (setting agent of the firm of Schering), 130 g of calcium stearate, 50 g of water and 2680 g of glass fibres are mixed as in Example 3 and processed to flexible sheeting.

Moulding of this sheet moulding compound under the same conditions as in Example 3 yields of objects with a good quality and surface.

Example 5

2000 g of phenolic resin (resole I of Example I), 335 g of Eurepox (epoxy resin of the firm of Schering), 85 g of Euredur (setting agent from Schering), 1100 g of gypsum anhydrite, 1100 g of Millicarb (filler of the firm of Plüss Staufer AG), 85 g of calcium stearate, 20 g of water and 1925 g of glass fibres are mixed as in Example 3 and processed to flexible sheet.

Moulding of this sheet moulding compound under the same conditions as in Example 3 yields objects with a good quality and surface.

Example 6

Preparation of bulk moulding compounds.

1100 g of phenolic resin (resole II of Example 2), 1230 g of gypsum anhydrite (product AB 20 of the firm of Bayer), 325 g of powdered quartz, 60 g of glass fibres with a length of ca. 2.5 cm, 35 g of calcium stearate, 220 g of 50% K_2CO_3 solution, 70 g of 50% NaOH solution and 35 g of MgO (thickener) are mixed as in Example 3. The compound obtained can be moulded according to the bulk moulding technique with good results.

Example 7

Preparation of dough moulding compounds.

1000 g of phenolic resin (resole II of Example 2), 1320 g of gypsum anhydrite (product AB 20 of the firm of Bayer), 555 g powdered quartz, 30 g of calcium stearate, 65 g of 50% NaOH solution and 55 g of glass fibres with a length of ca. 2.5 cm are mixed as in Example 3. The compound obtained can be moulded to objects according to the dough moulding technique with good results.

CLAIMS

1. Thermosetting resin composition on the basis of resole, filler and condensation catalysts, possibly with thickener(s), glass fibre and other usual additives, characterized in that at least a portion of the filler is a water-binding agent which does not become substantially water-binding until above a temperature of 50°C.

2. Thermosetting resin composition according to Claim 1, characterized in that it is in the form of a moulding compound.

3. Thermosetting resin composition according to Claim 2, characterized in that it is in the form of a BMC (bulk moulding compound), a DMC (dough moulding compound) or an SMC (sheet moulding compound).

4. Thermosetting resin composition according to any one of the Claims 1–3, characterized in that it contains at least 25 wt %. relative to the resole, of a filler that does not become essentially waterbinding until above 50°C.

5. Thermosetting resin composition according to any one of the Claims 1–4, characterized in that at least a portion of the filler is gypsum anhydrite.

6. Thermosetting resin composition according to Claim 5, characterized in that it comprises at least 50 wt %, relative to the resole, of gypsum anhydrite.

7. Thermosetting resin composition according to any one of the Claims 1–6, for application as a sheet moulding compound, characterized in that it is composed of
100 parts by weight of resole;
5–25 parts by weight of thickener;
25–200 parts by weight of gypsum anhydrite;
0–150 parts by weight of filler other than gypsum anhydrite;
0–20 parts by weight of water;
10–175 parts by weight of glass fibres;
0–15 parts by weight of condensation catalyst;
and, possibly, other usual additives.

8. Thermosetting resin composition according to any one of the Claims 1 through 6, for application as bulk or dough moulding compound, characterized in that it is composed of
100 parts by weight of resole;
0–20 parts by weight of thickener;
25–200 parts by weight of gypsum anhydrite;
0–150 parts by weight of filler other than gypsum anhydrite;
0–15 parts by weight of water;
0–25 parts by weight of glass fibres;
0–15 parts by weight of condensation catalyst;
and, possibly, other usual additives.

9. Moulded object from thermosetting material obtained by the setting, under pressure, of a thermosetting composition according to any one of the Claims 1–8.

10. Process substantially as described and/or explained by the examples.

Printed in the United Kingdom for Her Majesty's Stationery Office, Dd 8818935, 1985, 4235.
Published at The Patent Office, 25 Southampton Buildings, London, WC2A 1AY, from which copies may be obtained.